PHYSICAL REVIEW E **76**, 040801(R) (2007)

Cross-stream migration in dilute solutions of rigid polymers undergoing rectilinear flow near a wall

Joontaek Park, Jonathan M. Bricker, and Jason E. Butler[*]
Department of Chemical Engineering, University of Florida, Gainesville, Florida 32611, USA

(Received 27 July 2007; published 22 October 2007)

Kinetic theory is used to investigate cross-stream migration of a rigid polymer undergoing rectilinear flow in the vicinity of a wall. Hydrodynamic interactions between the polymers and the boundary result in a cross-stream migration. In simple shear flow, polymers migrate away from the wall, creating a depletion layer in the vicinity of the wall which thickens as the flow strength increases relative to the Brownian force. In pressure-driven flow, an off-center maximum in the center-of-mass distribution occurs due to a competition between hydrodynamic interactions with the wall and the anisotropic diffusivity induced by the inhomogeneous flow field.

DOI: 10.1103/PhysRevE.76.040801 PACS number(s): 83.80.Rs, 47.15.G−, 47.27.nd, 47.57.ef

Flexible polymers in dilute solution migrate across streamlines in simple shear and pressure-driven flows. Though the origin and direction of the migration were controversial [1], recent work [2–5] has clarified that flexible polymers primarily migrate away from bounding walls due to a hydrodynamic lift force. The local shear flow extends the polymer, generating tension in the chain and an additional flow field around the polymer. The flow field becomes asymmetric near a no-slip boundary and results in a net drift away from the wall for both simple shear and pressure-driven flow. In inhomogeneous flows, the variation in the local shear rate alters the position-dependent conformation and consequent diffusivity transverse to the flow. This additional mechanism results in a weak displacement of the polymers away from the centerline in pressure-driven flow, though the net migration still occurs away from the wall unless hydrodynamic interactions with the wall are screened, as occurs for highly confined polymers.

The mechanism and direction of migration remain unclear for rigid polymers in dilute solution. Measurements on semirigid xanthan molecules in pressure-driven flow indicate migration away from the wall, resulting in a depletion layer [6]. When considering only steric interactions with the walls, simulations of a rigid dumbbell predicted a limited increase of the depletion layer at sufficiently high shear [7]. However, mechanisms based on the anisotropic diffusivity predict a net migration of rigid polymers toward the wall in pressure-driven flow [8,9], similar to the mechanism for flexible polymers. Most recently, simulations of rigid polymers in pressure-driven flow predicted migration away from the wall [10], though the depletion layer is larger than predicted by steric interactions alone. The authors proposed that a subtle combination of orientation effects and hydrodynamic interactions with the walls produces the overall migration.

We develop a kinetic theory for the migration of a dilute solution of rigid polymers undergoing rectilinear flows and include hydrodynamic interactions with the bounding walls to confirm the results of Ref. [10] and clarify the origins of the observed migration. The theory contains approximations similar to those made for flexible polymers [2]: the polymer distribution function is factorized into a product of a center-of-mass and orientation distribution and a far-field approximation for the hydrodynamic interaction with the bounding wall is made. We first derive and present results for a rigid polymer undergoing simple shear flow near a single wall and show that rigid polymers migrate away from the wall due to hydrodynamic interactions with the wall. The theory is extended to pressure-driven flow between two bounding walls; in this case, we observe an off-center maximum in the center-of-mass distribution due to a competition between hydrodynamic interactions with the wall and the anisotropic diffusivity induced by the inhomogeneous flow field.

The evolution of a rigid polymer in solution (see Fig. 1) is governed by a continuity equation for the distribution function, $\Psi(\mathbf{r}_c,\mathbf{p},t)$, of the center-of-mass, $\mathbf{r}_c$, and orientation, $\mathbf{p}$,

$$\frac{\partial \Psi}{\partial t} = -\nabla \cdot (\dot{\mathbf{r}}_c \Psi) - \nabla_{\mathbf{p}} \cdot (\dot{\mathbf{p}} \Psi). \tag{1}$$

The probability distribution function is separated into a center-of-mass, n, and orientation distribution function ψ,

$$\Psi(\mathbf{r}_c,\mathbf{p},t) = n(\mathbf{r}_c,t)\psi(\mathbf{r}_c,\mathbf{p},t), \tag{2}$$

where $n(\mathbf{r}_c,t) = \int \Psi(\mathbf{r}_c,\mathbf{p},t) d\mathbf{p}$. Integrating Eq. (1) over $\mathbf{p}$ and solving for the steady result gives

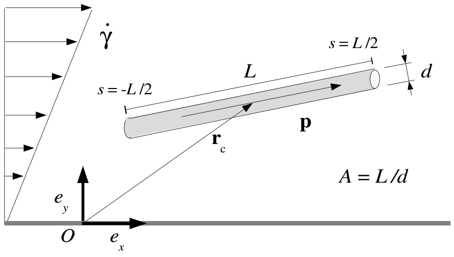

FIG. 1. A rigid polymer of length L and aspect ratio A suspended in a shear flow of strength $\dot{\gamma}$. The coordinate s describes positions along the polymer axis, and a no-slip boundary is located at $y=0$.

---

[*] butler@che.ufl.edu

1539-3755/2007/76(4)/040801(4)

$$\nabla \cdot (n\langle \dot{\mathbf{r}}_c \rangle) = \nabla \cdot \mathcal{J} = 0, \tag{3}$$

where angular brackets $\langle \cdots \rangle$ indicate an ensemble average over orientation, $\langle \dot{\mathbf{r}}_c \rangle = \int \dot{\mathbf{r}}_c \psi d\mathbf{p}$, and $\mathcal{J}$ is the polymer flux.

Solving Eq. (3) for the center-of-mass distribution requires the averaged center-of-mass velocity. In the absence of inertia and for a Newtonian suspending liquid, the velocity is determined by a balance between Brownian and hydrodynamic forces, where the hydrodynamic forces are approximated here by slender body theory [11]. At leading order, the center-of-mass velocity $\dot{\mathbf{r}}_c$ is related to the fluid velocity $\mathbf{u}(s)$ and the Brownian force $\mathbf{F}$ acting on the polymer by

$$\dot{\mathbf{r}}_c = \frac{1}{L}\int_{-L/2}^{L/2} \mathbf{u}(s) ds + \xi^{-1}(\mathbf{I} + \mathbf{pp}) \cdot \mathbf{F}, \tag{4}$$

where $\mathbf{I}$ is the identity matrix, $\xi^{-1} = \frac{\ln(2A)}{4\pi\mu L}$, and μ is the fluid viscosity. The Brownian force $\mathbf{F}$ is the integrated force distribution $\int_{-L/2}^{L/2}\mathbf{f}(s)ds$. The fluid velocity includes contributions from the imposed shear flow $\dot{\gamma}$ and the disturbance velocity generated by the force on the polymer which is reflected by the wall,

$$\mathbf{u}(s) = \dot{\gamma}(r_y + s p_y)\mathbf{e}_x + \int_{-L/2}^{L/2} \mathbf{G}(s,s') \cdot \mathbf{f}(s') ds', \tag{5}$$

where $\mathbf{G}(s,s')$ is the Green's function for a planar wall with the Oseen tensor removed [12]. The coordinate s' indicates the location of a point force on the polymer, whereas s is the point of evaluation of the reflected disturbance in velocity.

We linearize the force distribution using Legendre polynomials [13,14] and retain only the first two terms,

$$\mathbf{f}(s) = \frac{1}{L}\mathbf{F} + \frac{12s}{L^3}[\mathcal{T} \times \mathbf{p} + S\mathbf{p}], \tag{6}$$

where the Brownian torque $\mathcal{T} = \int_{-L/2}^{L/2} s\mathbf{p} \times \mathbf{f}(s) ds$ and the stresslet is given by

$$S = -\frac{\xi}{2L}\int_{-L/2}^{L/2} s\mathbf{p} \cdot \mathbf{u}(s) ds. \tag{7}$$

We also linearize $\mathbf{G}(s,s')$ about the center of the polymer under the assumption that the polymer is far from the wall $(r_y \gg L)$ [2]. Combining Eqs. (5) and (6), substituting the resulting expression for $\mathbf{u}(s)$ into Eq. (4), and eliminating the stresslet using Eq. (7) gives the center-of-mass velocity

$$\dot{\mathbf{r}}_c = \dot{\gamma} r_y \mathbf{e}_x + \dot{\gamma}\lambda(r_y)\mathcal{U} + \mathcal{M} \cdot \mathbf{F} + \mathcal{N} \cdot (\mathcal{T} \times \mathbf{p}), \tag{8}$$

where $\lambda(r_y) = \frac{L^3}{128\ln(2A)}\left(\frac{1}{r_y^2}\right)$. The vectors and tensors appearing in Eq. (8) are

$$\mathcal{U} = p_x p_y[(1 - p_y p_y)\mathbf{e}_y - 2p_y\mathbf{p}], \tag{9}$$

$$\mathcal{M} = \xi^{-1}(\mathbf{I} + \mathbf{pp}), \tag{10}$$

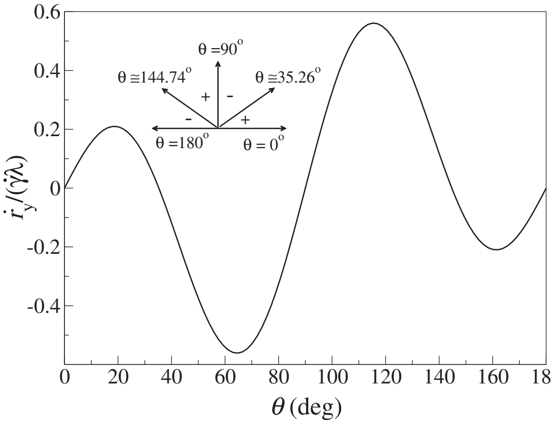

FIG. 2. Transverse velocity $\dot{r}_y$ as a function of polymer orientation $\theta = \cos^{-1}[p_x/(\sqrt{p_x^2 + p_y^2})]$, with $p_z = 0$. The inset shows the directional dependence on the polymer angle.

$$\mathcal{N} = \frac{3}{64\pi\mu}\left(\frac{1}{r_y^2}\right)[p_y(\mathbf{I} + \mathbf{e}_y\mathbf{e}_y) - \mathbf{e}_y\mathbf{p} + \mathbf{p}\mathbf{e}_y]. \tag{11}$$

Only the self-mobility has been retained for $\mathcal{M}$; additional terms resulting from interactions with the wall negligibly impact the final results.

The stresslet term within Eq. (6) couples the shear flow to a transverse motion. In this sense, the stresslet for the rigid polymer is analogous to the spring force in the theory for a flexible polymer; the inability of the rigid polymer to stretch or compress along its major axis generates an additional flow field within the fluid. This flow field is reflected by the wall and creates a transverse motion of the polymer. This contribution to the polymer motion appears in the second term of Eq. (8). Extracting the transverse component of the velocity resulting from the shear flow gives

$$\dot{r}_y = \dot{\gamma}\lambda(r_y)(p_x p_y)(1 - 3p_y p_y), \tag{12}$$

which matches previous results given without derivation [10]. Figure 2 shows $\dot{r}_y/\dot{\gamma}\lambda$ as a function of orientation with respect to the wall for a polymer in the plane of shear $(p_z = 0)$. For a force and torque-free polymer rotating in shear flow, Eq. (12) suggests that the center-of-mass will oscillate perpendicular to the wall [15,16]. The symmetry of the orientation distribution must be broken to produce a net velocity either away or towards the wall [16]. In the case of a rigid polymer, even very weak Brownian fluctuations break the symmetry.

To connect the orientation distribution with the polymer flux, Eq. (8) is ensemble averaged and multiplied by n to give

$$\mathcal{J} = n\dot{\gamma} r_y \mathbf{e}_x + n\dot{\gamma}\lambda(r_y)\langle \mathcal{U} \rangle + n\langle \mathcal{M} \cdot [-k_B T \nabla (\ln \Psi)] \rangle + n\langle \mathcal{N} \cdot [-k_B T \nabla_{\mathbf{p}}(\ln \Psi) \times \mathbf{p}] \rangle, \tag{13}$$

where $k_B T$ is the thermal energy and the Brownian forces and torques have been written in terms of the distribution function—i.e., $\mathbf{F} = -k_B T \nabla(\ln \Psi)$ and $\mathcal{T} = -k_B T \nabla_{\mathbf{p}}(\ln \Psi)$. Simplification of the third term in Eq. (13) gives

$$n\langle \boldsymbol{\mathcal{M}}\cdot[-k_BT\,\nabla(\ln\Psi)]\rangle = -k_BT\langle\boldsymbol{\mathcal{M}}\rangle\cdot\nabla n - nk_BT\,\nabla\cdot\langle\boldsymbol{\mathcal{M}}\rangle. \tag{14}$$

The fourth term in Eq. (13) becomes

$$n\langle\boldsymbol{\mathcal{N}}\cdot[-k_BT\nabla_{\mathbf{p}}(\ln\Psi)\times\mathbf{p}]\rangle = nk_BT\lambda(r_y)\left(\frac{72}{\xi L^2}\right)(\langle 2p_y\mathbf{p}+p_yp_y\mathbf{e}_y\rangle-\mathbf{e}_y). \tag{15}$$

Unlike the elastic dumbbell [2], the fourth term in Eq. (13) is nonzero, revealing an additional contribution to the migration of rigid polymers related to the Brownian torque. For fully developed flows and under the condition that the flux of the center-of-mass of the particles normal to the wall be zero, Eq. (3) becomes

$$\frac{\partial\ln n}{\partial r_y} = \frac{\lambda(r_y)}{L^2}[\mathrm{Pe}\alpha+72\beta] - \frac{\dfrac{\partial}{\partial y}\langle p_yp_y\rangle}{1+\langle p_yp_y\rangle}, \tag{16}$$

where the Péclet number is $\mathrm{Pe}=\frac{\xi L^2\dot{\gamma}}{k_BT}$. The contribution from the imposed shear flow due to including the stresslet is related to α,

$$\alpha = \left(\frac{\langle p_xp_y\rangle - 3\langle p_xp_yp_yp_y\rangle}{1+\langle p_yp_y\rangle}\right), \tag{17}$$

and the contribution arising from the Brownian torque is related to β,

$$\beta = \left(\frac{1-3\langle p_yp_y\rangle}{1+\langle p_yp_y\rangle}\right). \tag{18}$$

The last term in Eq. (16) corresponds to the contribution arising from the anisotropic diffusivity of a rigid polymer.

For a slender body in simple shear flow with Brownian torque, the orientation distribution at steady state is governed by

$$\nabla^2_{\mathbf{p}}\psi = \mathrm{Pe}_{\mathrm{r}}\nabla_{\mathbf{p}}\cdot[p_y(\mathbf{e}_x-p_x\mathbf{p})\psi], \tag{19}$$

where $\mathrm{Pe}_{\mathrm{r}}=\mathrm{Pe}/12$. We have assumed that rotation is not influenced by hydrodynamic or steric interactions with the wall. Also, a separation of the center-of-mass and rotational motions is implicit in Eq. (19), which assumes that the orientation distribution equilibrates much faster than the polymer migrates [2,8].

Equation (19) is solved numerically [17]; the resulting contributions of Peα and 72β to the center-of-mass distribution function are plotted in Fig. 3. The value of 72β approaches a limiting value of 72, whereas Peα increases indefinitely. Since the orientation moments are independent of position for simple shear flow, α and β are constants depending only on Pe and $\frac{\partial}{\partial y}\langle p_yp_y\rangle$ is zero. Integrating Eq. (16) gives

$$n(r_y) = exp\left[-\frac{L}{r_y}\left(\frac{\mathrm{Pe}\alpha+72\beta}{128\ln(2A)}\right)\right] \tag{20}$$

for a distribution which approaches a bulk value of 1 as y goes to infinity. Figure 4 shows that a net migration away from the wall exists at large Péclet numbers. The large depletion layer can exceed that predicted for rigid polymers at high Péclet numbers which interact with the bounding wall only through excluded volume [7]. The results in Fig. 4 are for $A=10$; polymers with higher aspect ratios will undergo a weaker migration as evident from the logarithmic dependence on A in Eq. (20).

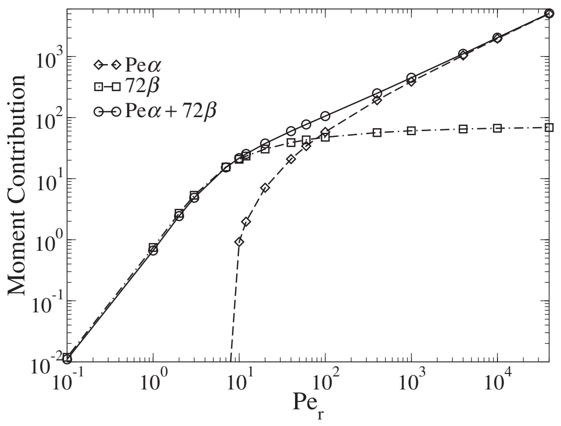

FIG. 3. Contribution of the shear flow (Peα) and Brownian torque (72β) to the migration of a rigid polymer in simple shear flow plotted as a function of Pe_{r}.

For simple shear flow, the differences in anisotropic diffusivity were ignored under the assumption that $\frac{\partial}{\partial y}\langle p_yp_y\rangle=0$; differences in diffusivity can influence the migration only weakly through steric effects near the wall. However, differences in diffusivity become important as a result of the inhomogeneous field in pressure-driven flow since $\langle p_yp_y\rangle$ becomes a function of position. To calculate the center-of-mass distribution of rigid polymers in pressure-driven flow, the effect from the two bounding walls is included by superposition [2]. Consequently, $\lambda(r_y)$ becomes $\frac{L^3}{128\ln(2A)}\left(\frac{1}{r_y^2}-\frac{1}{(H-r_y)^2}\right)$, where H is the height of the channel. Equation (16) is integrated numerically, with the orientation moments calculated from Eq. (19) at each position according to the local shear rate $\dot{\gamma}(r_y)=\frac{k_BT\overline{\mathrm{Pe}}}{\xi L^2}\left(1-\frac{2r_y}{H}\right)$, where $\overline{\mathrm{Pe}}$ is the Péclet number corresponding to the mean shear rate.

Figure 5 shows the results of the calculations for $A=10$. Near the center of the channel, where the shear rate is small,

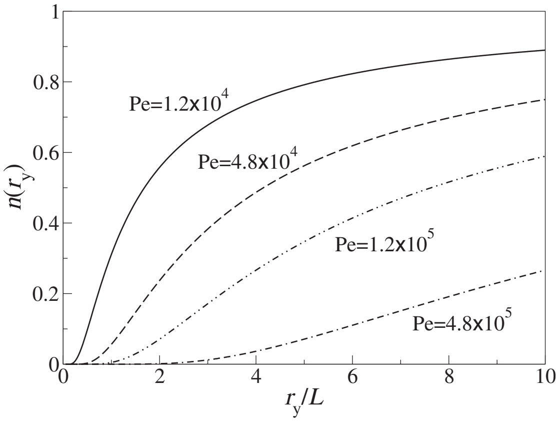

FIG. 4. Center-of-mass distribution for a rigid polymer with $A=10$ in simple shear flow.

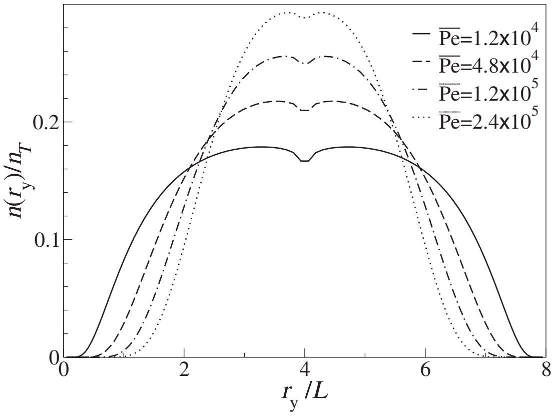

FIG. 5. Center-of-mass distribution for a rigid polymer with $A=10$ in pressure-driven flow. The height of the channel is $8L$ and $n_T=\int n dr_y$.

the contribution due to the anisotropic diffusivity results in a weak migration of polymers toward the wall. Specifically, $\langle p_y p_y \rangle$ decreases from a value of $1/3$ at the center of the channel and approaches zero near the wall. As a result, the migration is balanced by the hydrodynamic interactions of polymers with the boundaries to give an off-center maximum for $n(r_y)$. The effect of the anisotropic diffusivity becomes increasingly important relative to the wall interactions for polymers with larger aspect ratios. Consequently, the maximum value of $n(r_y)$ will move towards the wall as A increases.

The theoretical results for pressure-driven flow are similar to those from simulations which include hydrodynamic interactions with the wall [10]. When neglecting both steric and hydrodynamic interactions with the wall, however, a migration of polymers toward the wall is predicted for arbitrary values of Pe [8]. Similarly, under conditions of highly confined polymers coupled with weak pressure-driven flow, models which include steric wall effects [9] predict migration towards the wall. In these cases, the migration occurs solely because of the anisotropic diffusivity of the polymer as a result of the inhomogeneous flow field. Such a mechanism predicts no migration in simple shear flow where the orientation distribution is spatially uniform, contrary to our results. Furthermore, the qualitative difference in predicted migration in pressure-driven flow highlights the importance of including long-range hydrodynamic interactions.

To summarize, a kinetic theory has been developed for the migration of rigid polymers in rectilinear flows. Results from our theory are similar to results from theories describing flexible polymer systems which consider hydrodynamic interactions with the wall, despite differences in flexibility. For simple shear flow near a single wall, results indicate that hydrodynamic interactions with the wall cause a net cross-stream migration of polymers away from the wall. Results for pressure-driven flow, which include contributions from the anisotropic diffusivity of polymers, show an off-center maximum for the center-of-mass distribution. Though the theory presents general trends, improvements to the quantitative prediction can be made. For example, steric effects [9] as well as improvements to the wall interactions [18] can be included.

This work was supported by the National Science Foundation through a CAREER Award Grant No. (CTS-0348205).

---

[1] U. S. Agarwal, A. Dutta, and R. A. Mashelkar, Chem. Eng. Sci. **11**, 1693 (1994).
[2] H. Ma and M. D. Graham, Phys. Fluids **17**, 083103 (2005).
[3] R. Khare, M. D. Graham, and J. J. dePablo, Phys. Rev. Lett. **96**, 224505 (2006).
[4] O. B. Usta, J. E. Butler, and A. J. C. Ladd, Phys. Fluids **18**, 031703 (2006).
[5] O. B. Usta, J. E. Butler, and A. J. C. Ladd, Phys. Rev. Lett. **98**, 098301 (2007).
[6] D. Ausserre, J. Edwards, J. Lecourtier, H. Hervet, and F. Rondelez, Europhys. Lett. **14**, 33 (1991).
[7] J. J. de Pablo, H. C. Ottinger, and Y. Rabin, AIChE J. **38**, 273 (1992).
[8] L. C. Nitsche and E. J. Hinch, J. Fluid Mech. **332**, 1 (1997).
[9] R. L. Schiek and E. S. G. Shaqfeh, J. Fluid Mech. **332**, 23 (1997).
[10] D. Saintillan, E. S. G. Shaqfeh, and E. Darve, J. Fluid Mech. **557**, 297 (2006).
[11] G. K. Batchelor, J. Fluid Mech. **44**, 419 (1970).
[12] J. R. Blake, Proc. Cambridge Philos. Soc. **70**, 303 (1971).
[13] O. G. Harlen, R. R. Sundararajakumar, and D. L. Koch, J. Fluid Mech. **388**, 355 (1999).
[14] J. E. Butler and E. S. G. Shaqfeh, J. Fluid Mech. **468**, 205 (2002).
[15] R. Hsu and P. Ganatos, J. Fluid Mech. **268**, 267 (1994).
[16] P. Olla, Phys. Rev. Lett. **82**, 453 (1999).
[17] K. Asokan, T. R. Ramamohan, and V. Kumaran, Phys. Fluids **14**, 75 (2002).
[18] E. Barta and N. Liron, SIAM J. Appl. Math. **48**, 992 (1988).